

AF

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 11-292528

(43)Date of publication of application : 26.10.1999

(51)Int.Cl.

C01B 33/152
B01D 15/08
G01N 27/447
G01N 30/02
G01N 30/48
// C12N 11/14

(21)Application number : 11-010125

(71)Applicant : SOGA NAOHIRO
NAKANISHI KAZUKI
MRC:KK

(22)Date of filing : 19.01.1999

(72)Inventor : SOGA NAOHIRO
NAKANISHI KAZUKI
MIZUGUCHI HIROYOSHI

(30)Priority

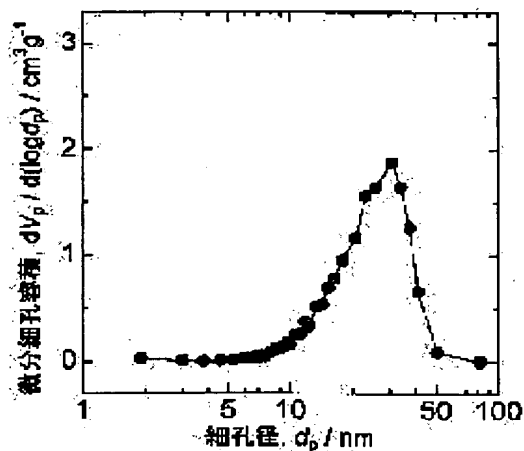
Priority number : 10 11377 Priority date : 23.01.1998 Priority country : JP

(54) PRODUCTION OF INORGANIC POROUS MATERIAL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a producing method of an inorg. porous material having a homogeneous structure with good reproducibility all over the area in a member having a narrow space such as a capillary and of between that plates, and consequently, which shows high separation performance when used for chromatography.

SOLUTION: A compd. to be pyrolyzed is preliminarily dissolved in a reaction soln. to prepare a gel by a solgel method in a member having a space of ≤ 1 mm distance. The gel consists of a solvent-rich phase having a three-dimensional mesh structure of ≥ 100 nm average diameter which is rich in the solvent, and a matrix phase which is rich in an inorg. material and has pores on the surface. Then the wet gel is heated to pyrolyze the low mol.wt. compd.



preliminarily dissolved in the preparing process of the gel, and then the gel is dried and heated.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

JAPANESE

[JP,11-292528,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE
INVENTION TECHNICAL PROBLEM MEANS EXAMPLE DESCRIPTION OF DRAWINGS
DRAWINGS

[Translation done.]

* NOTICES *

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] Dissolve the compound pyrolyzed beforehand in a reaction solution, and it sets in the member of 1 millimeter or less of gaps with a sol-gel method. By preparing the gel which consists of a frame phase which is rich in the solvent rich phase and mineral matter which are rich in the solvent which continued with an average diameter of 100 nanometers or more in the shape of a three-dimension mesh, and has pore on a front face, and heating the gel of a damp or wet condition continuously. The manufacture approach of the inorganic system porous body characterized by drying and heating gel after carrying out the pyrolysis of the compound beforehand dissolved in the reaction solution and making the fine structure of gel change.

[Claim 2] The manufacture approach of the inorganic system porous body which is made to carry out the pyrolysis of the compound beforehand dissolved in the reaction solution, and is characterized by to make the fine structure of gel change, to dry subsequently, and to heat after melting a water soluble polymer and the compound to pyrolyze to aqueous acids, adding the metallic compounds which have the functional group of hydrolysis nature in it, performing a hydrolysis reaction and a product's solidifying in the member of 1 millimeter or less of gaps.

[Claim 3] The manufacture approach of an inorganic system porous body according to claim 1 or 2 that the member of 1 millimeter or less of gaps is the thing and honeycomb which opposed the capillary tube or the plate of two or more sheets.

[Translation done.]

*** NOTICES ***

JPO and NCIPI are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach of an inorganic porous material. The manufacture approach of this invention is used suitable for manufacture of the capillary tube column for electrochromatography, the porosity for enzyme support, etc.

[0002]

[Description of the Prior Art] As this kind of a column for chromatographies, what was filled up with inorganic system bulking agents, such as silica gel, with physical means in the capillary tube is known. The column packing material used for electrochromatography needs to have the part which carried out the electric charge to the front face. Therefore, the inorganic system porosity which has a stable negative charge in neutral pH field, especially silica gel are used widely.

[0003] Generally minerals porous bodies, such as silica gel, are produced by the sol-gel method which is a liquid phase reaction. A sol-gel method generates the low molecular weight compound in which a polymerization is possible, and points out the thing of a general approach which finally obtains floc and a polymer. For example, hydrolysis of a metal salt or a coordination compound with hydrolysis of a metal chloride besides hydrolysis of a metal alkoxide, a carboxyl group, and the functional group of hydrolysis nature like beta-diketone and hydrolysis of metal amines are mentioned.

[0004] In order to prevent filling up an inorganic particle-like system bulking agent with a physical approach into a capillary tube generally, a particle's moving, and the column used for electrochromatography changing a restoration condition, it has been produced by the approach the components called a frit with comparatively low porosity stop the both ends of a capillary tube.

[0005]

[Problem(s) to be Solved by the Invention] However, the capillary tube column by particle restoration has the complicated restoration technique, and when requiring long duration, it is difficult for it to reproduce the restoration condition excellent in separability ability. Since uniform restoration of a particle becomes difficult by leaps and bounds as column length furthermore increases, it is hard to aim at improvement in the separability ability by increasing column length. Moreover, in the capillary tube column by particle restoration, in the space between a frit and a packed bed, air bubbles are produced in the sample solution and there is often a problem of reducing separability ability. Although the porous structure in the column decided by the restoration condition of a particle has effect strong against the separability ability of a capillary tube column, the approach of making a stable and uniform restoration condition with sufficient repeatability by the particle filling-up method is not yet established.

[0006] Then, when this invention person etc. inquires, it sets in members, such as a capillary tube with a bore of 1 millimeter or less, first. By producing gel with the solvent rich phase used as huge hole about 100 nanometers or more with a sol-gel method, and heating, without grinding the bulk-like gel of the damp or wet condition By carrying out the pyrolysis of the low molecular weight compound beforehand dissolved at the time of gel preparation, and becoming easy to dissolve a silica in the solvent which coexists with gel by this It turned out that it changes to the porous body of the duplex pore in which the wall of a huge hole had the narrow pore distribution which is a maximum of about 50 nanometers, and gel with this continuation porosity structure generates to

homogeneity covering the total die length of members, such as a capillary tube.

[0007] This invention is made based on such knowledge. The purpose gives not a low capillary tube column but pore structure with the main pore size for which it asks, and narrow distribution with sufficient repeatability, and, moreover, has the homogeneous structure where of repeatability is high, over the whole region in a capillary tube, and both the homogeneity and the repeatability which could not be avoided by the conventional particle filling-up method, and separability ability are to establish the manufacture approach of an inorganic system porous body of as a result giving high separability ability.

[0008]

[Means for Solving the Problem] The means dissolves the compound pyrolyzed beforehand in a reaction solution. With a sol-gel method The gel which consists of a frame phase which is rich in the solvent rich phase and mineral matter which are rich in the solvent which continued with an average diameter of 100 nanometers or more in the shape of a three-dimension mesh, and has pore on a front face By preparing in the member of 1 millimeter or less of gaps, and subsequently heating the gel of a damp or wet condition, the pyrolysis of the compound in which it was made to dissolve beforehand at the time of gel preparation is carried out, and it is characterized by drying and heating gel.

[0009] In this means, the case where make mineral matter into a silica SiO_2 , and the compound which is made to live together beforehand and to pyrolyze is used as amide system compounds, such as a urea changed into basicity, for acidity or alkalinity by the pyrolysis is desirable.

[0010] Similarly the means of the above-mentioned purpose achievement melts a water soluble polymer and the compound to pyrolyze to aqueous acids. After adding the metallic compounds which have the functional group of hydrolysis nature in it, performing a hydrolysis reaction and a product's solidifying in the member of 1 millimeter or less of gaps, by subsequently heating the gel of a damp or wet condition The pyrolysis of the low molecular weight compound beforehand dissolved at the time of gel preparation is carried out, and it is characterized by drying subsequently and heating.

[0011] Water soluble polymers are the water solution of suitable concentration, and a water-soluble organic macromolecule which can be accomplished theoretically here. Be [what is necessary / just although it may dissolve in homogeneity into the system of reaction containing the alcohol generated with the metallic compounds which have the functional group of hydrolysis nature] Sodium salt or potassium salt of polystyrene sulfonate which is specifically a giant-molecule metal salt, The polyacrylic acid which is a macromolecule acid, dissociates and serves as the poly anion, the poly allylamine which is a macromolecule base and produces the poly cation in a water solution, and polyethyleneimine, Or the polyvinyl pyrrolidone which has a carbonyl group is suitable for the polyethylene oxide which is a neutral giant molecule and has ether linkage in a principal chain, and a side chain. Moreover, it may replace with an organic macromolecule, a formamide, polyhydric alcohol, and a surfactant may be used, and the glycerol of polyoxyethylene alkyl ether is the optimal in that case as a surfactant as polyhydric alcohol.

[0012] As metallic compounds which have the functional group of hydrolysis nature, a metal alkoxide or its oligomer can be used and, as for these things, what has few carbon numbers, such as a methoxy group, an ethoxy radical, and a propoxy group, is desirable. Moreover, as the metal, the metal of the oxide finally formed, for example, Si, Ti, Zr, and aluminum, is used. As this metal, you may be one sort or two sorts or more. On the other hand as oligomer, it can specifically be used for alcohol to 10 **** extent at homogeneity that what is necessary is just what can carry out dissolution distribution.

[0013] Moreover, as aqueous acids, the thing of 0.01 or more mol concentration of organic acids, such as a thing of 0.001 or more mol concentration of mineral acids, such as a hydrochloric acid and a nitric acid, or an acetic acid, and a formic acid, is usually desirable.

[0014] With the member of 1 millimeter or less of gaps, it is constituted by a capillary tube, the plate of two sheets, the honeycomb, etc., and, in the case of a capillary tube, a gap is equivalent to a bore, and when [of two sheets] monotonous, it is equivalent to opposed monotonous spacing. These capillary tubes, a plate, etc. consist of silica glass, and a gap is 30-200 micrometers preferably. Moreover, when using a plate, 0.3-10mm in thickness, 3-500mm wide, and 3-500mm long of the size of the monotony itself are desirable. Moreover, a plate is not limited to two sheets but may

create two or more facing each other and two or more gaps one by one. Furthermore, the number of the gaps in a honeycomb is not limited, either. A multi-capillary tube is producible by using the plate of two or more of these sheets, and a honeycomb. Moreover, two or more capillary tubes may be tied up into a knot.

[0015] In hydrolysis, it can attain by saving a solution at the room temperature of 40-80 degrees C in a capillary tube etc. for 0.5 to 5 hours. Hydrolysis passes through the process which a solution transparent at the beginning becomes cloudy, produces phase separation with a water soluble polymer, and is gelled at last. A water soluble polymer is in a distributed condition in this hydrolysis process, and those precipitate is not produced substantially.

[0016] As a concrete example of the compound of the pyrolysis nature made to live together beforehand, since the pH values of the solvent after heating are important conditions as it is shown also in the example mentioned later, although organic amides, such as a urea or a hexamethylenetetramine, a formamide, N-methyl formamide, N,N-dimethylformamide, an acetamide, N-methyl acetamide, and N,N-dimethylacetamide, can be used, if it is the compound which makes a solvent basicity after a pyrolysis, there will be especially no limit. Although the pyrolysis nature compound made to live together is based also on the class of compound, they are [as opposed to / in the case of a urea / 10g of reaction solutions] 0.1-0.7g preferably 0.05-0.8g, for example. Moreover, in the case of a urea, heating temperature is 40-200 degrees C, and, as for the pH value of the solvent after heating, 6.0-12.0 are desirable. Moreover, what produces a compound with the property to dissolve a silica like a hydrofluoric acid by the pyrolysis can be used similarly.

[0017] As a method of producing the inorganic porosity which can control pore structure most effectively in this invention, a metal alkoxide can be used as a start raw material, the suitable quality of a concomitant can be added in a raw material, and the sol-gel method which produces and cheats out of structure with the solvent rich phase used as a huge hole can be mentioned. The suitable quality of a concomitant is matter with the work which carries out induction of sol-gel transition and the phase separation process to coincidence, and it gels at the same time this separates into a solvent rich phase and a frame phase. The surfactant containing the giant molecule or polyoxyethylene chain which melts into a solvent like polyethylene oxide as quality of a concomitant is desirable.

[0018] A water soluble polymer is melted to aqueous acids, and if the metallic compounds which have the functional group of hydrolysis nature in it are added and a hydrolysis reaction is performed, the gel divided into the solvent rich phase and the frame phase in the member of 1 millimeter or less of gaps will generate. After a product (gel) solidifies and passing through suitable maturing time, by heating the gel of a damp or wet condition, the amide system compound beforehand dissolved in the reaction solution pyrolyzes, and pH of the solvent in contact with the internal surface of a frame phase rises. And a solvent corrodes the internal surface and pore size is gradually expanded by changing the concave convex voice of an internal surface. Although the degree of change is very small in acidity or a neutral region, in the case of the gel which uses a silica as a principal component, the part which constitutes pore dissolves, and the reaction to which average pore size becomes large comes to occur in it notably by re-depositing into a flatter part as a pyrolysis prospers and the basicity of a water solution increases.

[0019] At gel only with the pore restricted in three dimension without the huge hole, also by the part which may dissolve as an equilibrium condition, since quality of an effluent cannot be spread even in an external solution, the original pore structure remains at a considerable rate. On the other hand, in gel with the solvent rich phase used as a huge hole, there is much pore which is not restricted two-dimensional, since an exchange of the matter with an external water solution takes place sufficiently frequently, small pore disappears in parallel to development of large pore, and the whole pore volume distribution does not spread notably.

[0020] In addition, in a heating process, it is effective that put gel on the bottom of a sealing condition, the vapor pressure of a pyrolysate is saturated, and pH of a solvent takes a stationary value promptly.

[0021] Since the heating processing time required in order that the dissolution and a re-deposit reaction may reach a steady state and may acquire the pore structure corresponding to this changes with the magnitude of a huge hole, or the volume of a sample, it needs to determine the shortest processing time from which pore structure will not change substantially in each processing

condition.

[0022] The gel which finished heat-treatment turns into desiccation gel stuck to the tube wall in the member of 1 millimeter or less of gaps by making a solvent evaporate. In this desiccation gel, since the quality of a concomitant in a start solution may remain, the inorganic target system porous body can be obtained by heat-treating at suitable temperature and pyrolyzing the organic substance etc. In addition, desiccation is left at 30-80 degrees C for several hours to dozens hours, and is performed, and heat treatment is heated at about 200-800 degrees C.

[0023]

[Example] - Example 1 - Polyethylene oxide (Aldrich quotient lot number number 85,645-2) 0.90g and 0.90g of ureas which are a water soluble polymer first were dissolved in 10g of centinormal acetic-acid water solutions, it is under stirring about tetramethoxy silane 4ml, in addition the hydrolysis reaction was performed in this solution. After agitating several minutes, the obtained transparence solution was sealed in the capillary tube with a bore of 0.1 millimeters (100 micrometers), and when held in the 40-degree C incubator, it solidified after about 30 minutes.

[0024] The solidified sample was ripened for several [further] hours, and it kept at 120 degrees C under sealing conditions for 1 hour. At this time, the pH value of the solvent which coexists with gel was about 10.7. Gel was dried for three days at 40 degrees C after this processing, and it heated to 400 degrees C with the programming rate of 100 degrees C/h. The porous body which consists of amorphous silica into a capillary tube with a bore of 0.1 millimeters by this was obtained.

[0025] Existing in the obtained porous body with the structure with which the through tube to which 2 micrometer (= 2000nm) extent of diameters of a feed hole was equal became entangled in the shape of a three-dimension mesh was confirmed by electron microscope observation of the cross section of a capillary tube column. And it was confirmed by nitrogen adsorption measurement that much pores with a diameter of about 25nm exist in the wall of the through tube. A pore-volume-distribution curve is shown in drawing 1.

[0026] In addition, although hole distribution of a through tube did not change when the porous body was manufactured on the same conditions as the above except having changed the retention temperature under sealing conditions to 80 degrees C or 200 degrees C, the main pore size measured by the nitrogen adsorption process changed to about 15nm or 50nm, respectively. This showed that such main large pore size was obtained that the heating temperature of gel is high.

[0027] The capillary tube column of 25cm of effective length obtained by the above-mentioned approach was attached in electrochromatography equipment, and thiourea was detected with the applied voltage of 20kV in 20 degrees C using the mobile phase of acetonitrile:tris-buffers hydrochloric-acid 50mM=80:20 and pH=8.

[0028] The linear velocity of the electroendosmose style produced under above-mentioned conditions became 1.19 mm/s, and became a value almost equivalent to the capillary tube column which is used conventionally and by which particle restoration was carried out good. The elution peak of the thiourea under these conditions and the value of a current and an electrical potential difference are shown in drawing 2. The theoretical plate number calculated from peak width was about 48000 steps to 25cm, and this was the value of the capillary tube column with which it filled up good equivalent in about 200,000 steps/[m and].

[0029] - Example 2 - The porous body was manufactured on the same conditions as an example 1 except having set to 0.45g the amount of the urea made to live together, and having set the pH value to 9. Then, in the heating temperature of 80 degrees C of gel, 120 degrees C, and 200 degrees C, although main pore size was set to 15nm, 25nm, and 50nm, respectively, and it was in agreement by case [of an example 1], and experimental error within the limits and was hardly dependent on the concentration of a urea, the size of the pore volume distribution measured by the differential distribution curve became large in any case. The pore volume distribution of the porous body obtained became narrow, and it turned out that pore volume becomes large, so that the concentration of the urea made to live together was raised from this. Moreover, it was possible to have performed electrochromatography analysis equivalent to an example 1 also with the capillary tube column obtained by the above-mentioned approach.

[0030] - Example 3 - Polyethylene oxide (Aldrich quotient lot number number 85,645-2) 0.90g and 0.90g of ureas which are a water soluble polymer first were dissolved in 10g of centinormal acetic-

acid water solutions, it is under stirring about tetramethoxy silane 4ml, in addition the hydrolysis reaction was performed in this solution. After agitating several minutes, it sealed in the gap of two slide glass which opposed the obtained transparence solution at intervals of 0.1 millimeters (100 micrometers), and when held in the 40-degree C incubator, it solidified after about 30 minutes. The solidified sample was ripened for several [further] hours, and it kept at 120 degrees C under sealing conditions for 1 hour. At this time, the pH value of the solvent which coexists with gel was about 10.7. Gel was dried for three days at 40 degrees C after this processing, and it heated to 400 degrees C with the programming rate of 100 degrees C/h. By this, the sheet metal-like porous body which was stuck to two slide glass of 0.1 millimeters of gaps and which consists of amorphous silica was obtained.

[0031] Existing in the obtained porous body with the structure with which the through tube to which 2 micrometer (= 2000nm) extent of diameters of a feed hole was equal became entangled in the shape of a three-dimension mesh was confirmed by electron microscope observation of the cross section of a sheet metal-like sample. And it was confirmed by nitrogen adsorption measurement that much pores with a diameter of about 25nm exist in the wall of the through tube. The pore-volume-distribution curve was the same as that of drawing 1.

[0032] In addition, although hole distribution of a through tube did not change when the porous body was manufactured on the same conditions as the above except having changed the retention temperature under sealing conditions to 80 degrees C or 200 degrees C, the main pore size measured by the nitrogen adsorption process changed to about 15nm or 50nm, respectively. This showed that such main large pore size was obtained that the heating temperature of gel is high.

[0033] The sheet metal-like column of 25cm of effective length obtained by the above-mentioned approach was attached in the electrophoresis apparatus, and migration of thiourea was performed with the applied voltage of 20kV in 20 degrees C using the mobile phase of acetonitrile:tris-buffers hydrochloric-acid 50mM=80:20 and pH=8. The linear velocity of the electroendosmose style produced under above-mentioned conditions became a value almost equivalent to the electrophoresis gel which serves as 0.6 mm/s and consists of polymer gel used conventionally.

[0034] - Example 4 - The porous body was manufactured on the same conditions as an example 3 except having set to 0.45g the amount of the urea made to live together, and having set the pH value to 9. Then, in the heating temperature of 80 degrees C of gel, 120 degrees C, and 200 degrees C, although main pore size was set to 15nm, 25nm, and 50nm, respectively, and it was in agreement by case [of an example 3], and experimental error within the limits and was hardly dependent on the concentration of a urea, the size of the pore volume distribution measured by the differential distribution curve became large in any case. The pore volume distribution of the porous body obtained became narrow, and it turned out that pore volume becomes large, so that the concentration of the urea made to live together was raised from this. Moreover, it was possible to have performed electrophoresis analysis equivalent to an example 3 also with the sheet metal-like column obtained by the above-mentioned approach.

[0035]

[Effect of the Invention] According to this invention, the porous body controlled by desired pore distribution in the member of 1 millimeter or less of gaps can be manufactured as mentioned above. And since it is the porous body of the duplex pore structure of a huge hole and pore, it is applicable to electrochromatography as the one apparatus capillary tube column which does not need restoration actuation, a sheet metal-like column, etc.

[Translation done.]